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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: Joseph L. Haberfeld, Edward C. Hsu & Julian F. Johnson (1973): Liquid Crystal Purification by Zone Refining, Molecular Crystals and Liquid Crystals, 24:1-2, 1-5

To link to this article: http://dx.doi.org/10.1080/15421407308083383

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Molecular Crystals and Liquid Crystals. 1973. Vol. 24, pp. 1–5
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Liquid Crystal Purification by Zone Refining†‡

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Received September 28, 1972*; in revised form December* 4, 1972

Abstract—A series of nematic liquid crystals which had been solvent recrystallized was further purified by use of the technique of zone refining. In all cases purity increased. Purity was determined using differential scanning calorimetry. Purity differences when the zone refiner was used at mesophase temperatures and isotropic liquid temperatures were studied.

A comparison of the results from this study with those of other investigators is given, and the implications concerning thermodynamic measurements on liquid crystals are discussed.

1. Introduction

The technique of purification by zone refining is well established for organic compounds$^{(1)}$ but has had little attention for liquid crystals. There are some discrepancies in the thermodynamic data of liquid crystals. This work was done to determine the degree of purification produced by zone refining for liquid crystals and particularly the effect on transition temperatures.

2. Experimental

The zone refining was carried out using a Fisher zone refiner (Pittsburg, Pa.) with 4 mm I.D. glass tubing as a sample vessel. The rate of travel of the heater was always 2.4 in/hr. Purities were established using a Perkin–Elmer DSC-1B (Norwalk, Conn.) and the calculation method of Plato and Glasgow.$^{(2)}$ The values quoted for purity in Table 1 are not absolute values but are used comparatively.

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† Part XXXV of a series on Order and Flow of Liquid Crystals.

‡ Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

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TABLE 1 Comparative Purities of *p*-Azoxyanisole Zone Refined after Solvent Recrystallization

Fraction	Isotropic liquid zone mole % purity	Mesophase zone mole % purity	Non-recrystallized zone refined mole % purity
1st	99.961	99.951	99.931
2nd	99.996	99.963	99.956
3rd	99.933	99.954	99.897
4th	99.948	99.909	99.705
5th	99.876	99.913	99.777

Original solvent recrystallized PAA = 99.940 mole % purity.
Original non-recrystallized PAA = 99.872 mole % purity.

The precision of the numbers quoted is higher than the measurements justify but is used for illustrative purposes only.

Small differences are readily observable by looking at the DSC traces. Figure 1 shows two traces, the top one for 99.48 mole % PAA and the bottom for 99.93 mole % PAA. Correction factors for nonlinearity of the temperature versus $1/F$ plot where F is the

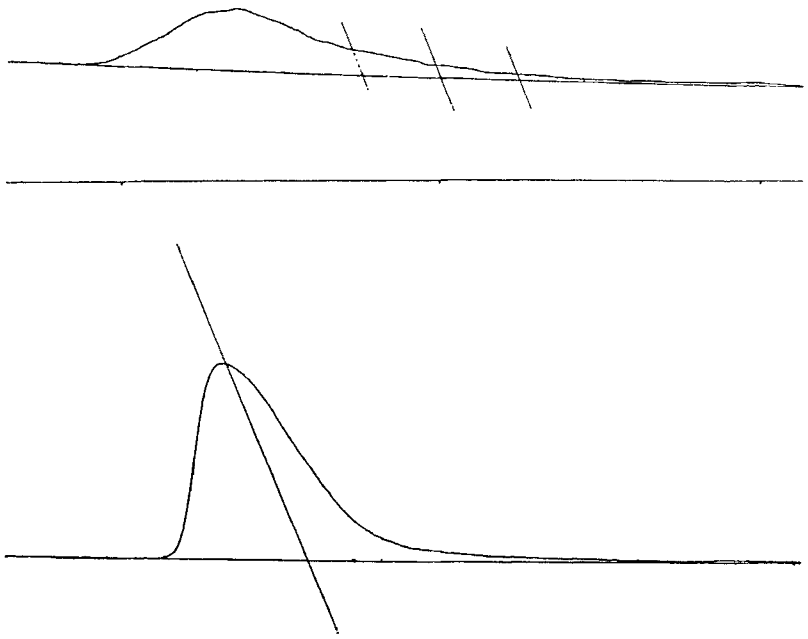

Figure 1. Differential scanning calorimetric measurements on para-azoxyanisole. Top 99.48 mole %; Bottom 99.93 mole %.

fraction of area at any given temperature, were calculated by the method of Sondak.(3)

The *p*-azoxyanisole was obtained from the Aldrich Chemical Co. (Milwaukee, Wis.) and found to be 99.87 mole % pure. Three successive recrystallizations were done from absolute ehtanol with the final purity being 99.40 mole%. On the table the second portion in every case was the most pure showing that impurities travel in both directions. In general if the sample goes through enough passes the third section should be most pure. The isotropic liquid zones and the mesophase zone samples were each given 12 passes with one heater. The efficiency of purification was evaluated for two cases, in the first the liquid zone was at a temperature such that liquid zone was in the isotropic phase and the second in the nematic phase. The mesophase zone temperature was approximately in the middle of the range and the isotropic liquid zone was at 2–5 degrees above the transition. The increase in viscosity in the mesophase sample caused less efficient purification as expected due to mass transfer considerations,(4) thus equivalent purity is not obtained by running in the mesophase.

The non-recrystallized column is material directly from the sample as received. The zone refiner was operated for 16 passes with two heaters and again showed increasing purity.

The changes in heats and temperatures of transitions are illustrated in Table 2. The temperatures were measured by a Dupont 900 Differential Thermal Analyzer (Wilmington, Del.) using the DSC cell. The heating rate was 5°/min. The heats of transition were done on the Perkin–Elmer DSC-1B with a heating rate of 0.625°/min and a range of 2, the same conditions which were used for the purity determination.

The temperatures of transition are somewhat higher than those previously reported, see Table 2, which is consistent with a higher purity. The heats of transition which should not change materially with impurities of the same chemical nature did not change. The precision of the heats of transition are of the order of ± 3%.

Table 3 shows the purities and comparable thermodynamic data for the homologous series following *p*-azoxyanisole. In all but one case the temperature of transition increases with zone refining and for that one it remained the same.

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TABLE 2 Comparison of the Thermodynamic Data on the Transitions of *p,p'*-Azoxyanisole

Trans. type	Trans. temp. °C	Trans. heat cal/mole	Trans. entropy cal/mole/° K	Ref.
Solid-Nematic	119.5	7230	18.4	This work
Nematic-Isotropic	136.5	168	0.41	
Solid→Nematic	117.5	7260	18.6	
Nematic→Isotropic	134.2	181	0.444	
Solid II→Nematic	104.4	5630	14.9	5
Nematic→Solid II	76	7230	20.7	
Solid II→Solid I	61	1030	3.09	
Solid→Nematic	117.5	6800	17.4	6
Nematic→Isotropic	134.0	150	0.37	
Solid→Nematic	118.2	7067	18.07	
Nematic→Isotropic	135.3	137.2	0.3360	7
Nematic→Isotropic	135.3 extrapolated	164.9	0.4039	
Solid→Nematic	117.6	7440	19.0	8
Nematic→Isotropic	133.9	176	0.432	
Solid→Nematic	117	7280	18.7	
Nematic→Isotropic	128 onset	178	0.444	9
Nematic→Isotropic	132 sharp break	178	0.440	
Nematic→Isotropic	132	462	1.14	10, 11
Nematic→Isotropic	132	176	0.434	12
Nematic→Isotropic	132	183	0.453	12
Solid→Nematic	118	7700	19.7	12
Nematic→Isotropic	132	176	0.434	

TABLE 3 Comparative Purities, Transition Temperatures and Transition Heats

		Transition temperatures and Transition heats			
	Comparative	Solid→Nematic		Nematic→Isotropic	
Compound	purity mole%	T° C	ΔH cal/gm	T° C	ΔH cal/gm
p-Azoxyphenetole					
(Recrystallized)	99.51	137.3	22.39	167.2	1.60
(Recrystallized & zone refined)	99.96	137.5	22.86	167.8	1.77
p,p'-n-Dipropoxyazoxybenzene					
(Recrystallized)	98.92	117.0	19.06	121.5	0.71
(Recrystallized & zone refined)	99.49	118.3	20.51	124.0	0.88
p,p'-n-Dibutoxyazoxybenzene					
(Recrystallized)	99.56	105.8	14.46	136.2	1.20
(Recrystallized & zone refined)	99.83	105.8	14.58	136.6	1.21
p,p'-n-Dihexyloxyazoxybenzene					
(Recrystallized)	99.06	78.8	23.50	127.2	1.08
(Recrystallized & zone refined)	99.57	79.6	24.32	128.0	1.23

Recrystallized is 3 times from absolute ethanol.

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3. Conclusions

Zone refining offers a simple, convenient technique for materially increasing the purity of liquid crystals over the more commonly used solvent recrystallization. Twelve passes at 2.4 in/hr and at a temperature slightly above the nematic-isotropic liquid transition gives a 20% fraction of very high purity.

Acknowledgements

A portion of this research was supported by the University of Connecticut Research Foundation.

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